

## FTIR and Mössbauer spectroscopic studies of archaeological potteries from Nathikudi, Tamil Nadu

R Venkatachalapathy\*, D Gournis<sup>1</sup>, C Manoharan, S Dhanapandian and K Deenadayalan

Department of Physics (DDE), Annamalai University, Annamalainagar-608 002, Tamil Nadu, India

<sup>1</sup>Department of Materials Science and Engineering, University of Ioannina, GR-45110, Greece

E-mail : venkatr5@rediffmail.com

Received 29 April 2004, accepted 9 September 2004

**Abstract** : Fourier Transform Infrared (FTIR) and room temperature Mössbauer spectra have been recorded for the recently excavated archaeological potteries from Nathikudi, Tamil Nadu, India. The experimental results explore the technology involved in producing the archaeological artifacts for different purposes. During firing, the iron present in the clay materials undergoes characteristic change in its chemical and physical state, depending on the kiln atmosphere and the maximum firing temperature reached, which can be followed by using FTIR and Mössbauer spectroscopic techniques. From the above techniques, type of clay, firing temperature and firing atmosphere for the production of archaeological potteries were well established.

**Keywords** : Archaeological potteries, FTIR, Mössbauer, firing temperature.

**PACS Nos.** : 33.20.Ea, 33.45.+x

### 1. Introduction

The recently excavated South Indian archaeological potteries collected from Nathikudi (NTI) (Lat. 9°26'N; Long. 77°42'E) were subjected to spectroscopic studies. The representative pottery samples NTI-1 (red ware), NTI-2 (black ware) were studied by using FTIR and Mössbauer spectroscopy. The archaeomagnetic dating of the above samples were established which belongs to 800–1000 AD [1]. The technology of production of archaeological materials reveal the level of the technical background of the artisans and can be used as an index of ancient civilizations and their interactions [2]. FTIR spectroscopy has been for decades, a frequently used method to investigate the structure, bonding and chemical properties of clay minerals [3]. On firing the clay materials, the thermal transformation takes places and these can be followed by FTIR technique [4]. The microscopic analysis of the iron (state of iron *i.e.* Fe<sup>2+</sup>/Fe<sup>3+</sup>, and iron oxides) bearing minerals can be carried out by Mössbauer spectroscopy, which is used in the determination of

oxidation state of Fe-content, firing temperature, firing conditions and colouring mechanism [5].

### 2. Experimental details

The FTIR absorption spectra were recorded in the frequency region 4000–400 cm<sup>-1</sup>, using model Paragon 500, Perkin-Elmer spectrophotometer with 16 scan mode by using standard KBr pellet technique. The accuracy of the measurement is  $\pm 4$  cm<sup>-1</sup> in 4000 to 2000 cm<sup>-1</sup> region and  $\pm 2$  cm<sup>-1</sup> in 2000 to 400 cm<sup>-1</sup> region. The Mössbauer measurements were performed in conventional constant acceleration spectrometer. Spectra were recorded at room temperature and fitted on a PC with a least square minimization procedure, assuming Lorentzian line shapes.

### 3. Results and discussion

#### 3.1. FTIR studies :

The FTIR spectra recorded for the local clay (NTI-clay) in as-received state and refired to different

\*Corresponding Author

temperatures under laboratory conditions are shown in Figure 1. band centered around  $1030\text{ cm}^{-1}$  with asymmetry around  $915\text{ cm}^{-1}$  indicates the substitution of Al in the sheet

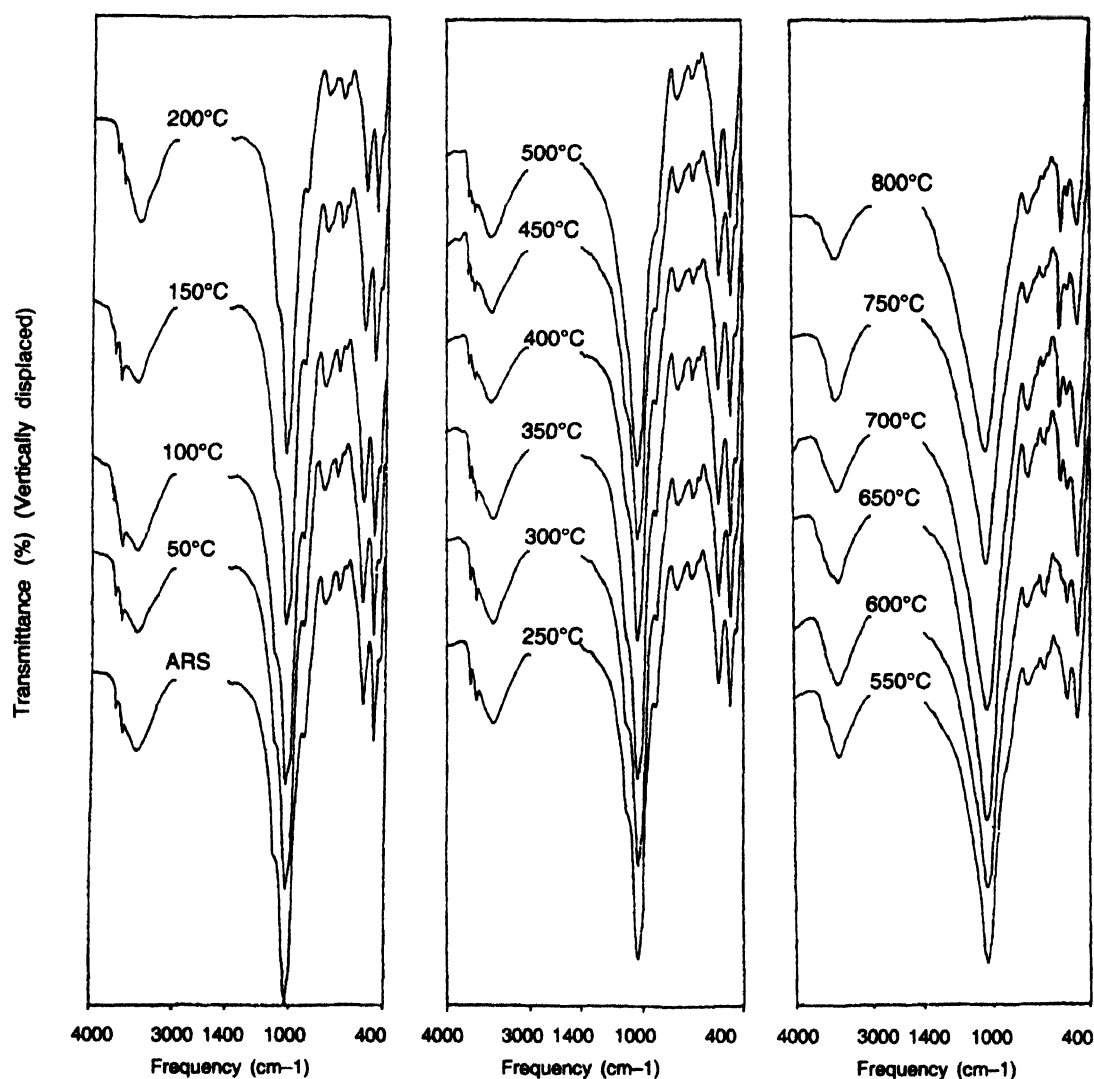


Figure 1. FTIR absorption spectra of local clay (NTI-clay).

The absorption bands at  $3700$  and  $3620\text{ cm}^{-1}$  in the local clay reveal that the type of clay is disordered kaolinite and the same is also established by the weak shoulder at  $915\text{ cm}^{-1}$  which is due to the substitution of aluminium in octahedral sheet [6]. On firing the clay in steps of  $50^\circ\text{C}$ , all the above bands exist with decrease in intensity around  $300^\circ\text{C}$ , and disappear at  $550^\circ\text{C}$ . Wagner *et al* [7] reported the firing temperature of archaeological potteries as above  $450^\circ\text{C}$  during manufacturing, from the absence of the bands at  $3700, 3620$  and  $915\text{ cm}^{-1}$ . The presence of weak broad bands at  $3440$  and  $1640\text{ cm}^{-1}$  indicates the presence of absorbed water molecules. For the present sample, these bands persist upto  $800^\circ\text{C}$ , which is due to the water molecules absorbed from the atmospheric air while recording the spectra. A broad

structure [8]. A broad symmetry band centered around  $1030\text{ cm}^{-1}$  indicates that the destruction of octahedral sheet structure have taken place around  $650^\circ\text{C}$ . The presence of the above band in as-received state spectra of the clay, indicates that the type of clay is red. The sharp bands appeared at  $795$  and  $775\text{ cm}^{-1}$  along with  $695\text{ cm}^{-1}$  in all the samples, are due to the presence of quartz [9]. The band at  $640\text{ cm}^{-1}$  is attributed to Al-O coordination vibration. The Si-O-Al bending vibration observed at  $530\text{ cm}^{-1}$  is the most sensitive band to the presence of residual Al in the octahedral sheet [10]. Maniatis *et al* [2] reported that during firing, no perceptible changes are observed in this region up to  $450^\circ\text{C}$ ; above this temperature, the iron replaces the aluminium, the decrease in intensity of the band at  $530\text{ cm}^{-1}$  is attributed to

hematite along with weak shoulder at  $580\text{ cm}^{-1}$  attributed to magnetite. At  $800^\circ\text{C}$ , the absorption bands at  $580$  and  $540\text{ cm}^{-1}$  become sharp with increase in intensity of the band at  $580\text{ cm}^{-1}$  indicating that it is due to oxidation and crystallization of hematite. The band at  $470\text{ cm}^{-1}$  due to Si-O band is free from any temperature effects,

The FTIR spectra of NTI-1 and NTI-2 in the as-received state and refired to  $300$ ,  $500$  and  $800^\circ\text{C}$ , are shown in Figure 2. The spectra of the pottery samples NTI-1 and NTI-2 show absorption bands at  $3450$  and  $1640\text{ cm}^{-1}$  attributed to absorbed water molecules that gets diminished in intensity at  $300^\circ\text{C}$  due to the evaporation of water molecules. The absence of  $3700$  and  $3620\text{ cm}^{-1}$  bands along with  $915\text{ cm}^{-1}$ , indicates the destruction of inner hydroxyl and octahedral sheet in the case of NTI-1 and NTI-2, thus showing that these samples were fired above  $450^\circ\text{C}$ . When clay is fired above  $600^\circ\text{C}$ , the silicate structure collapses and a broad symmetry

band is observed at  $1030\text{ cm}^{-1}$  for red clay and at  $1080\text{ cm}^{-1}$  for white clay [8]. In the above two samples, a broad symmetry band observed at  $1030\text{ cm}^{-1}$ , indicates that the samples were made of red clay type, and were subjected to a firing temperature of above  $600^\circ\text{C}$  during manufacturing.

In the case of sample NTI-1, the intensity of the band at  $580\text{ cm}^{-1}$  is more than that of  $540\text{ cm}^{-1}$ , and the intensity remains same up to  $500^\circ\text{C}$ . The increase in intensity of the band at  $580\text{ cm}^{-1}$  at  $800^\circ\text{C}$  indicates that further oxidation sets in during refiring. From the above observation, it was found that the sample was fired under oxidizing atmospheric condition with firing temperature of around  $650^\circ\text{C}$ , where as in the case of sample NTI-2, weak shoulder observed at  $580$  and  $540\text{ cm}^{-1}$  in the as-received state remains same up to  $300^\circ\text{C}$ . At  $500$  and  $800^\circ\text{C}$ , the intensity of the band at  $580\text{ cm}^{-1}$  increases while  $540\text{ cm}^{-1}$  remains as a weak shoulder. The increase

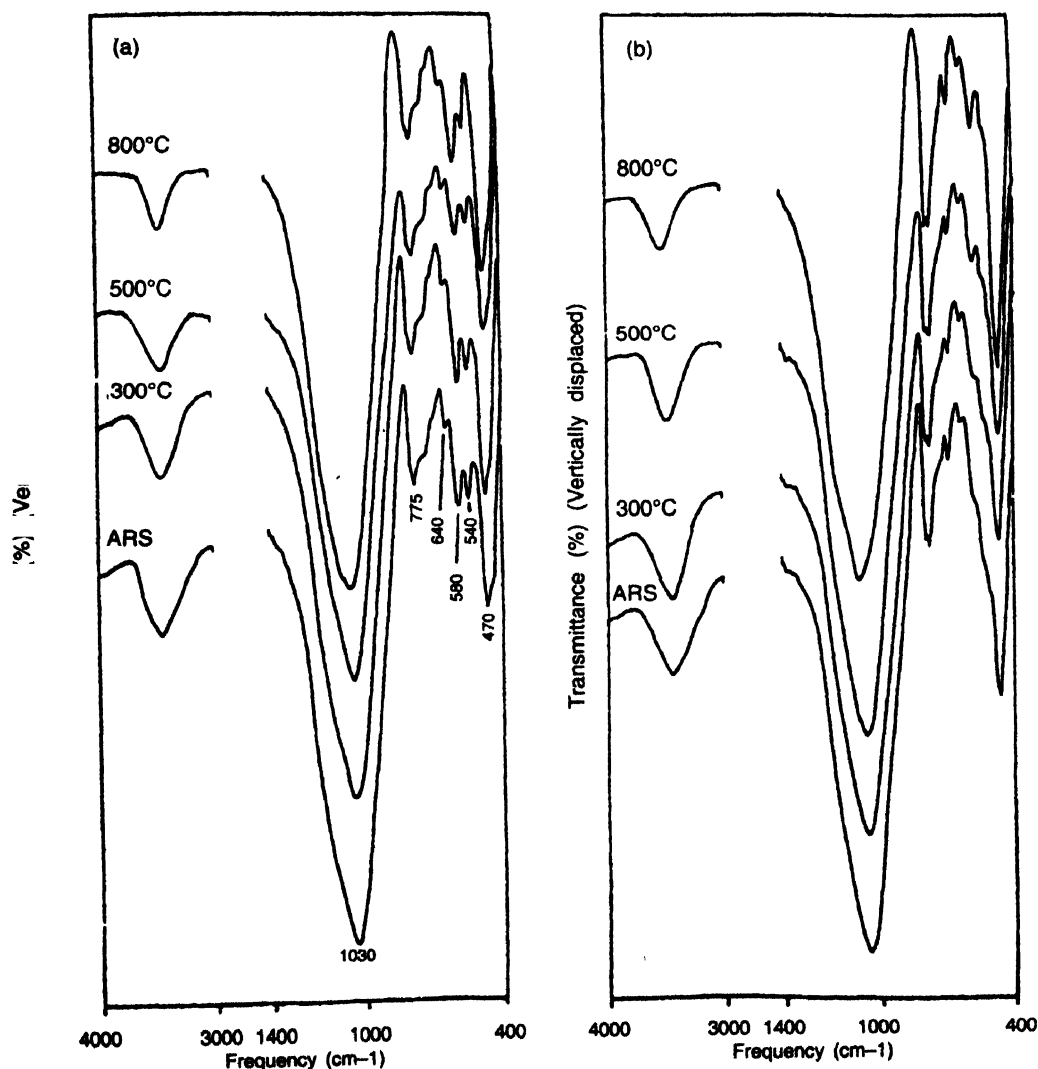


Figure 2. FTIR absorption spectra of pottery samples (a) NTI-1 and (b) NTI-2.

in intensity of the band  $580\text{ cm}^{-1}$  at  $500^\circ\text{C}$  indicates that oxidation of iron takes place. A sharp and intense band at  $580\text{ cm}^{-1}$  has been observed at  $800^\circ\text{C}$  which indicates the complete oxidation of iron compounds. From the above observation, it is clear that the samples were fired under strong reducing atmospheric condition above  $600^\circ\text{C}$  for a long period, which can be established from the black colour of the pottery. The presence of bands at  $580$  and  $540\text{ cm}^{-1}$  as weak shoulders in as-received state, may be due to iron dissolved in water during burial, which gets oxidized at  $500^\circ\text{C}$ . By comparing the FTIR spectra of the above potteries with the local clay, it is found that all the potteries were made up of local clay *i.e.* red clay. The FTIR spectra of sample NTI-1 refired at  $650^\circ\text{C}$  is similar to local clay fired at  $650^\circ\text{C}$  which indicates that the above sample (NTI-1) was fired around  $650^\circ\text{C}$  under oxidizing condition. In the other sample, the absence of the prominent bands at  $540$  and  $580\text{ cm}^{-1}$  reflects the reduced atmospheric firing of the artifacts.

### 3.2. Mössbauer studies :

Room temperature Mössbauer spectra were recorded for the samples NTI-1 and NTI-2 in the as-received state and are shown in Figure 3. The Mössbauer parameters were derived from the peak positions of the spectra.

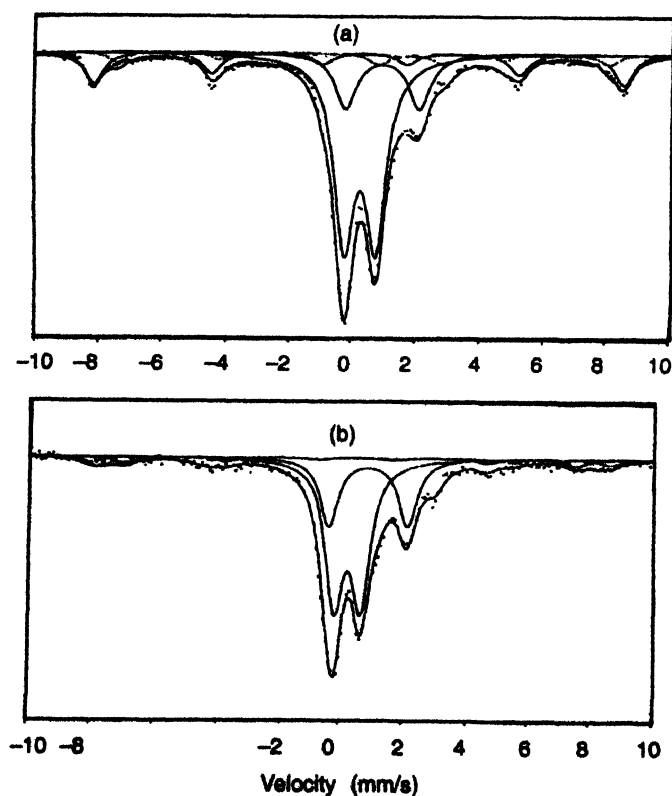


Figure 3. Room temperature Mössbauer spectra of pottery samples in the as-received state (a) NTI-1 and (b) NTI-2.

From the presence/absence of paramagnetic  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , the firing condition, firing temperature and colouring mechanisms of the archaeological potteries have been deduced. The decrease/disappearance of  $\text{Fe}^{2+}$  ion indicative of oxygen-rich in original firing atmosphere. The observed Mössbauer spectrum of pottery sample NTI-1 exhibits characteristic of presence of large quantity of paramagnetic  $\text{Fe}^{3+}$  and minimum of  $\text{Fe}^{2+}$  along with six line pattern. The observed isomer shift ( $\delta$ )  $0.371\text{ mm/s}$  and quadrupole splitting ( $\Delta$ )  $1.250\text{ mm/s}$  are attributed [11] to paramagnetic  $\text{Fe}^{3+}$  ions. The observed parameters ( $\delta = 1.046\text{ mm/s}$  and  $\Delta = 2.293\text{ mm/s}$ ) are attributed [11] to paramagnetic  $\text{Fe}^{2+}$  ions. An important point to be noted that the observed parameters ( $\delta = 0.388\text{ mm/s}$  and  $\Delta = 0.20\text{ mm/s}$ ) along with the effective magnetic hyperfine field of  $514\text{ kOe}$  are attributed to well-crystallized and magnetically-ordered hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) present in the sample [12]. These values are in agreement with the reported values of isomer shift of  $0.205\text{ mm/s}$ , quadrupole splitting of  $-0.21 \pm 0.03$  and hyperfine field value [13] of  $518 \pm 6\text{ kG}$  for  $\alpha\text{-Fe}_2\text{O}_3$ . From the above information, one can confirm that this pottery might have been fired under oxidizing condition. It is well established from the red colour of the pottery. From the above information and the observed quadrupole splitting value of  $\text{Fe}^{3+}$  ( $1.250\text{ mm/s}$ ), one can confirm the firing temperature of this sample as around  $700^\circ\text{C}$  during manufacturing. Wagner *et al* [14] reported that usually the quadrupole splitting value of  $\text{Fe}^{3+}$  exhibits a typical increase from  $0.7$  to  $1.4\text{ mm/s}$  on firing at  $300\text{--}700^\circ\text{C}$  and a decrease in value above  $800^\circ\text{C}$ .

The Mössbauer spectrum of the pottery sample NTI-2 shows the presence of almost equal amount of paramagnetic  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions. The observed parameters ( $\delta = 0.369\text{ mm/s}$  and  $\Delta = 0.850\text{ mm/s}$ ) are attributed to the presence of  $\text{Fe}^{3+}$  ions and the values ( $\delta = 0.994\text{ mm/s}$  and  $\Delta = 2.470\text{ mm/s}$ ) are attributed to the presence of  $\text{Fe}^{2+}$  ions. The presence of equal amount of  $\text{Fe}^{2+}$  indicates that this pottery might have been fired under reducing atmospheric condition and air was not allowed during the entire firing cycle. It is well established from the black colour of the pottery.

### 4. Conclusion

From FTIR studies, the pottery samples collected from Nathikudi (NTI-1, NTI-2) were made of red clay type. Firing temperature and firing conditions of the above samples are established. NTI-1 was fired from  $650\text{--}700^\circ\text{C}$  during manufacturing under oxidizing atmosphere. NTI-2 was fired above  $600^\circ\text{C}$  under reducing atmospheric

condition. The oxidation state of iron like  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and hematite are identified from the Mössbauer spectra. From the state of iron, the firing condition followed by the artisans during manufacturing, their art of controlling firing temperature and colouration of the artifacts were well established. The results were compared with local clay.

### Acknowledgment

The authors are thankful to Mr. V Balachandran, Thiruthangal, for having provided the archaeological potteries.

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